Phonon self-energy effects due to superconductivity in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$

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Raman scattering of $A_{1g}$ phonons in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ single crystals ($\delta=0.13$, $T_c=86$ K) has been measured as a function of temperature. We report an anomalous softening in the frequency and a decrease in the linewidth of the $A_{1g}$ phonon at 290 cm$^{-1}$ ($O_{12}$ c-axis in-phase vibration) below $T_c$. We also confirm a smaller anomalous softening in the frequency of the $A_{1g}$ phonon at 465 cm$^{-1}$ ($O_3$ c-axis vibration), but for this phonon mode no linewidth anomaly has been found. We compare the anomalous softening and linewidth behavior in the superconducting state with theoretical calculations for isotropic s-wave, planar d-wave, and $d_{x^2-y^2}$ gap symmetries and as for a layered superconductor model. [S0163-1829(97)09837-8]

I. INTRODUCTION

The temperature dependence of phonon frequencies and linewidths near $T_c$ continue to attract a considerable interest in the high-temperature superconductors (HTSC’s) because phonon self-energy effects due to superconductivity can be studied. The dependence of the phonon self-energy on the electronic states above and below $T_c$ has been widely used to estimate the value of the superconducting energy gap in the YBa$_2$Cu$_3$O$_{7-\delta}$ (Y123),$^1$ YBa$_2$Cu$_4$O$_8$ (Y124),$^2$ and Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi2212) (Ref. 3) compounds. Experimentally, these phonon anomalies in HTSC’s were observed by studying the Raman spectra of YBa$_2$Cu$_3$O$_{7-\delta}$. A recent study of the oxygen isotope effect on $A_{1g}$ phonons in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$, which the ions of the CuO$_2$ planes participate. We report in this paper a study of the temperature dependence of the $A_{1g}$ phonon modes at 290 cm$^{-1}$ and 465 cm$^{-1}$ in Bi2212 single crystals.

The remainder of this paper is organized as follows. In Sec. II, the experimental techniques are described. In Sec. III, polarized Raman spectra for different temperature are presented for the 290 and 465 cm$^{-1}$ vibrational modes, and results for the temperature dependence of the frequency and linewidth are reported. Section IV discusses the interpretation of the results based on the strong-coupling theory and finally the conclusions of this work are presented in Sec. V.

II. EXPERIMENTAL TECHNIQUES

The Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ single crystals were grown by a conventional self-flux method employing a double crucible.$^9$ Quantitative chemical analysis by means of wavelength-dispersion spectroscopy (WDS) showed the composition of the crystals to be Bi$_{12.15}$Sr$_{1.90}$Cu$_{0.96}$O$_{28.8}$. The superconducting transition temperature was determined by four-probe resistance measurement yielding a $T_c$ of 86 K. Raman scattering experiments were carried out in backscattering geometry. The single-crystal platelets, oriented with the $a$- $b$ plane normal to the incident beam, were mounted with silver paint on the cold finger of a closed-cycle Displex He refrigerator. The temperature in the sample chamber was controlled by resistive heating of the cold finger. To measure and regulate the temperature in the range from 10 to 300 K we used an Artonix controller and an Au-Cr thermocouple. The laser light from an argon-ion laser operating at 514.5 nm was used as the excitation source. The laser power incident on the sample was kept at 5 mW and the collection time for each run was 60 min. The collected Raman signal was dispersed by a Jobin-Yvon (T64000) spectograph and detected with a charge-coupled device (CCD) camera. During each series of measurements the grating position was kept fixed and centered at the phonon frequency under investigation. This pro-
procedure was necessary to avoid a possible error in the measured Raman frequency due to slight movement of the grating.

III. RESULTS

Polarized Raman spectra for the $Z(YY) - Z(A_{1g})$ symmetry from the $a$-$b$ plane of a single crystal of Bi$_{2.15}$Sr$_{1.90}$Ca$_{0.96}$Cu$_{2.0}$O$_{8+\delta}$ were collected for single crystals form different batch at temperatures in the range 10–300 K. In Fig. 1 we show the Raman spectra of the $A_{1g}$ mode at 465 cm$^{-1}$ at three different temperatures. This phonon has been assigned to the $c$-axis vibration of O$_3$ atoms in the strontium layers.\textsuperscript{9,10} Two peaks at 458 and 465 cm$^{-1}$ are observed in Fig. 1. In order to better isolate the temperature dependence of the frequency and linewidth of the main peak (465 cm$^{-1}$) we have used a double Lorentzian fitting, keeping constant the parameters for the lower intensity mode at 458 cm$^{-1}$.

FIG. 1. Raman spectra of $A_{1g}$ phonons at 465 cm$^{-1}$ in Bi$_{2.15}$Sr$_{1.90}$Ca$_{0.96}$Cu$_{2.0}$O$_{8+\delta}$ single crystals with $\delta = 0.13$ and $T_c = 86$ K taken at 10, 100, and 300 K. The temperature dependence of the frequency and linewidth of the main peak at 465 cm$^{-1}$ was fitted using a double Lorentzian, keeping constant the parameters for the lower intensity mode at 458 cm$^{-1}$.

FIG. 2. Temperature dependence of the frequency of the $Z(YY) - Z(A_{1g})$ phonon at 465 cm$^{-1}$ in Bi$_{2.15}$Sr$_{1.90}$Ca$_{0.96}$Cu$_{2.0}$O$_{8+\delta}$ with $T_c = 86$ K taken for different samples represented by triangles and squares. In the superconducting state the frequency shows an anomalous softening of about $\Delta \omega / \omega = -0.5\%$.

\begin{equation}
\gamma(\omega, T) = a_1 [1 + 2 n(\omega / 2T)] + a_2, \tag{1}
\end{equation}

where $n$ is the Bose factor, $a_1$ and $a_2$ are constants, and $\omega_p$ is the frequency of the mode. The best fit to the data was

FIG. 3. Temperature dependence of the linewidth of the $A_{1g}$ phonon at 465 cm$^{-1}$ in Bi$_{2.15}$Sr$_{1.90}$Ca$_{0.96}$Cu$_{2.0}$O$_{8+\delta}$ with $T_c = 86$ K. The dashed line is derived from a calculation of the anharmonic decay of two phonons with opposite $q$ vectors, each having a frequency close to $\omega_p / 2$ [Eq. (1)].
achieved with the fitting parameters $a_1 = 9.02 \text{ cm}^{-1}$, $a_2 = 4.95 \text{ cm}^{-1}$, and $\omega_p = 465 \text{ cm}^{-1}$.

In Fig. 4 we present a typical Raman spectrum with $Z(YY) - Z$ polarization of the 290 cm$^{-1} A_{1g}$ mode for three different temperatures. Besides the 290 cm$^{-1}$ mode, another $A_{1g}$ mode at 327 cm$^{-1}$, corresponding to the $c$-axis vibration of the oxygen ($O_{1,2}$) atoms in the Bi layer, is also observed. The phonon near 290 cm$^{-1}$ has been identified as the $c$-axis in-phase vibration of the $O_{1,2}$ atoms in the CuO$_2$ layer. We notice that even the 285 cm$^{-1} B_{1g}$ is also active in $YY$ polarization, and it is not detected in Fig. 4. This phonon is much weaker than the 290 cm$^{-1} A_{1g}$, and it can be seen with appreciable intensity in $X'Y'$ scattering geometry [where $X' = (1/\sqrt{2}) (1, 1)$ and $Y' = (1/\sqrt{2}) (1, -1)$].

In order to account for any mutual interference between the 290 and 327 cm$^{-1}$ modes we used a combined fitting procedure to obtain the values of their frequencies and linewidths. A Lorentzian profile was used to fit the symmetric line shape of the 327 cm$^{-1}$ mode and a Fano line shape profile was used to fit the slightly asymmetric line shape of the 290 cm$^{-1}$ mode. Therefore, the Raman intensity is given by

$$I(\omega) \propto \frac{(e + q)^2}{1 + e^2} + B + \text{Lorentzian},$$

where $e = (\omega - \omega_p)/\gamma$, $\omega_p$ is the phonon frequency, $q$ is the asymmetry parameter, and $B$ is a linear extrapolated background $[B = B_0 + 0.0012(\omega - 250)]$ between 250 and 330 cm$^{-1}$. The dashed line in Fig. 4 is the result of applying this fitting procedure to the spectrum at 10 K. The fitting parameters for the Fano mode are $q = -5.81$, $\omega_p = 300.6 \text{ cm}^{-1}$, and $\gamma = 11.91 \text{ cm}^{-1}$ and that for the Lorentzian mode are $\omega = 329.0 \text{ cm}^{-1}$ and $\gamma = 27.46 \text{ cm}^{-1}$. The $|q|$ value is nearly constant ($\approx 3$) above $T_c$, but below $T_c$ it increases, reaching a value of $|q| \approx 6$ at 10 K. Anomalies of the $q$ parameters at $T_c$ have been reported in Y124. The frequencies of the 290 cm$^{-1}$ mode obtained at different temperatures for three different samples are plotted in Fig. 5. Above $T_c$ and below 200 K, the frequency behavior is similar to that found in Y124 by Heynen et al., while below $T_c$ a softening in the frequency of about $\Delta \omega/\omega \approx -1.3\%$ is observed.

In Fig. 6 the linewidth of the 290 cm$^{-1}$ mode is plotted as a function of the temperature. The dashed line corresponds to the anharmonic decay fitted with Eq. (1), using $a_1 = 8.26 \text{ cm}^{-1}$, $a_2 = 3.25 \text{ cm}^{-1}$, and $\omega_p = 290 \text{ cm}^{-1}$. Once again, above $T_c$, the phonon linewidth is consistent with the anharmonic decay profile, but below $T_c$, the phonon linewidth shows a narrowing of about 6 cm$^{-1}$. The onset of the frequency softening and the linewidth decrease occurs about 15 K above the value of $T_c$ determined by dc magnetization measurements. An even higher temperature difference was found in the Y123 compounds.

### IV. DISCUSSION

Group theoretical analysis of Bi2212 based on a tetragonal cell (space group $I4/mmm$) predicts 14 Raman-active...
Zeyher and Zwicknagl\textsuperscript{13} have shown that, if the electron-phonon coupling is strong enough, the phonon should soften or harden below $T_c$, depending on whether the phonon frequency is less than or greater than twice the superconducting gap energy. The superconductivity-induced change in the frequency of the $\nu$ phonon is given by\textsuperscript{13}

$$\Delta \omega_\nu / \omega_\nu = \lambda_e \text{Re}(\Sigma_\nu)/2N, \quad (3)$$

where $\lambda_e$ is the electron-phonon coupling constant for the $\nu$ phonon, $N$ is the normal density of states per spin at the Fermi energy $E_F$, and $\Sigma_\nu$ is the complex self-energy for the $\nu$ phonon. Moreover, the phonon linewidth should decrease or increase below $T_c$, depending on whether the phonon energy is less than or greater than twice the superconducting gap, respectively. The phonon linewidth change $\Delta \Gamma_\nu$ is given by\textsuperscript{13}

$$\Delta \Gamma_\nu / \omega_\nu = -\lambda_e \text{Im}(\Sigma_\nu)/2N. \quad (4)$$

The curves for the real and imaginary parts of the phonon self-energy and the changes of phonon frequency and linewidth for different temperatures and impurity scattering rates are presented in Figs. 3–6 of Ref. 13. The most drastic effects should occur when $\omega \approx 2\Delta$, where $\Delta$ is the superconducting gap. The physical reason why the phonon linewidth changes in the superconducting state is that superconductivity reduces the number of possible electronic decay channels for phonons with energy less than twice the gap, resulting in a decrease of phonon linewidth, while phonons with energy greater than twice the gap experience an increase in the quasiparticle scattering, resulting in an increase of phonon linewidth. Similarly, since energy levels of interacting excitations tend to repel phonons with energies greater than the gap we expected to harden, while phonons with energies less than the gap we expected to soften below $T_c$. These effects would be expected in the clean limit. However, in the dirty limit, with $1/(2\Delta \tau) = 3$, where $\tau$ is the scattering time, the hardening for phonons with energy above the gap may turn into a slight softening and the expected broadening will decrease by approximately 80%. This shows that in the strong-coupling limit the effects of softening and broadening will depend on $T/T_c$ and also on the impurity scattering rate $1/(2\Delta \tau)$.

Nicol $et$ $al.$\textsuperscript{14} have calculated the frequency shift and the change in linewidth, in the clean limit, due to superconductivity in the high-$T_c$ superconductors assuming a $d$-wave pairing interaction. They have also presented a more general model of a superconductor with nodes in the gap function and related it both to the $d$-wave model and to a model for layered superconductors. In the layered superconductor model the anisotropic gap function is given by $\Delta_k = \Delta [1 + b \cos(k_x)]$, where $b$ is the anisotropy parameter. Therefore, for $b = 0$ the standard $s$-wave result is recovered. However, for $b \neq 0$, in contrast to the usual isotropic $s$-wave picture, there are three regions of behavior: (i) Phonons with energy less than twice the minimum gap value will...
soften with no change in linewidth, (ii) phonons between twice the minimum and the maximum gaps will soften and broaden, and finally, (iii) phonons with energy greater than twice the maximum gap will broaden and harden. The broadening in the intermediate region is explained because in superconductors with nodes in the gap function, particle-hole pairs can be created at arbitrarily low energy (at the nodes) and contribute to scattering. Therefore, experimental results with broadening and softening could be a signature of a gap parameter that exhibits nodes.

Devereaux\textsuperscript{15} has studied the temperature dependence below $T_c$ of the line shapes of optical phonons of different symmetry. He found that phonons with $A_{1g}$ and $B_{1g}$ symmetry couple differently to the electrons. As a consequence, the real and imaginary parts of the phonon self-energy peak at $\omega/2\Delta \approx 1$ for $B_{1g}$ symmetry and $\omega/2\Delta \approx 0.5$ for $A_{1g}$ symmetry. He shows that in the case of $d_{x^2-y^2}$ pairing symmetry, phonons of $B_{1g}$ symmetry ($285$ cm$^{-1}$) with energy below the peak in the imaginary part of the self-energy could have a substantial narrowing below $T_c$. On the other hand, phonons with $A_{1g}$ symmetry ($465$ cm$^{-1}$) which lie above the peak in the imaginary part of the self-energy should not show any linewidth anomaly.

Previous results from electronic Raman scattering\textsuperscript{16} (ERS) measured above and below $T_c$ in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ single crystals with $\delta=0.13$ ($T_c=86$ K) provide evidence that the gap is anisotropic and that its energy for the $A_{1g}$ symmetry is close to $2\Delta=385$ cm$^{-1}$. Assuming that this is the true gap value in this symmetry for the slightly doped samples of Bi$_2$2212, this means that the phonon modes at $290$ and $465$ cm$^{-1}$ studied in this work are below and above twice the gap energy, respectively. Therefore, the normalized optical phonon frequency is given by $\omega/2\Delta \approx 0.77$ and $1.2$ for the $290$ and $465$ cm$^{-1}$ $A_{1g}$ phonons, respectively.

Analyzing our experimental results based in the Zeyher’s model for the isotropic $s$ wave we would expect that below $T_c$ and in the clean limit, the $290$ cm$^{-1}$ mode will exhibit softening and narrowing, whereas the $465$ cm$^{-1}$ mode will exhibit hardening and broadening. The prediction of softening and narrowing of the $290$ cm$^{-1}$ mode below $T_c$ is consistent with our experimental results. However, the prediction of hardening and broadening below $T_c$ is inconsistent with the softening and no change in the linewidth found for the $465$ cm$^{-1}$ mode. However, if the impurity scattering rate plays an important role, with $1/(2\Delta \tau)=3$, the hardening of the phonons above $2\Delta$ can become a small softening (see Fig. 5 from Ref. 13), and the expected broadening will decrease by a factor of 4 compared to the clean limit.

Another possibility is that the pairing interaction has $d$-wave energy-gap symmetry as proposed by Nicol \textit{et al.}\textsuperscript{14} In Fig. 7 of Ref. 14 is plotted a comparison between the experimental data and the theoretical curves for three models: isotropic $s$-wave, planar $d$-wave, and a layered anisotropic superconductor model with $2\Delta_{mn}=2\Delta_0(1+b)$ and $2\Delta_{max}=2\Delta_0(1+b)$ where $\Delta_0=\Delta(T=0)$ and assuming for the anisotropy parameter $b=0.125$ and $2\Delta_0=380$ cm$^{-1}$. Note that the phonon mode at $290$ cm$^{-1}$ is below twice the minimum gap, $[2\Delta_0(1-b)=332$ cm$^{-1}$], and so according to Fig. 7 of Ref. 14, in the clean limit softening is predicted by each of the three models presented. However, the linewidth should not change in either the isotropic $s$-wave or the layered superconductor model, whereas for the planar $d$-wave model broadening of the $290$ cm$^{-1}$ phonon is predicted. The agreement of these models with our experimental result for the $290$ cm$^{-1}$ mode is good for the frequency shift but not for the linewidth, since none of them predicted the observed narrowing of the linewidth below $T_c$. The phonon at $465$ cm$^{-1}$ is above twice the maximum gap ($2\Delta_0(1+b)=427$ cm$^{-1}$), and so according to Fig. 7 of Ref. 14 we should expect below $T_c$ a hardening and broadening, which is inconsistent with the softening without apparently change in the linewidth that was reported in Refs. 6 and 7 and confirmed by the present experimental result.

Devereaux\textsuperscript{15} has discussed the experimental results for the linewidth in Bi2212 and Y123, assuming a $d_{x^2-y^2}$ gap symmetry. He concluded that the behavior of the linewidth at $T_c$ of both phonons could be explained by his approach; i.e., the $285$ cm$^{-1}$ ($B_{1g}$) and the $465$ cm$^{-1}$ ($A_{1g}$) does not show any appreciable change. He based his analyses on the different low-temperature dependence of the imaginary part of the self-energy for the $A_{1g}$ (linear dependence) and $B_{1g}$ ($T^2$ dependence) channels. However, the linewidth narrowing that we found for the $290$ cm$^{-1}$ $A_{1g}$ could not be explained by the Devereaux analysis.

V. CONCLUSIONS

We have measured the superconductivity-induced changes in the frequency and linewidth of the $A_{1g}$ Raman-active phonons at $290$ and $465$ cm$^{-1}$ in several single crystals of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$. We found that in the superconducting state the $A_{1g}$ phonon mode at $290$ cm$^{-1}$ softened and narrowed, whereas the $A_{1g}$ mode at $465$ cm$^{-1}$ softened with no detectable change in its linewidth. We compare the anomalous softening and linewidth behavior observed in the superconducting state with the theoretical predictions for isotropic $s$-wave, planar $d$-wave, a layered superconductor model, and $d_{x^2-y^2}$ gap symmetries. We found that none of those theoretical predictions could account for our results regarding the narrowing of the $A_{1g}$ $290$ cm$^{-1}$ phonon mode. However, many experimental results have shown that the $d_{x^2-y^2}$ state is a viable candidate for the pairing state of this high-$T_c$ superconductor. Since our experiment was carried out with a close optimally doped sample ($\delta=0.13$ and $T_c=86$ K), more Raman measurements with overdoped and underdoped samples could contribute to understanding the symmetry of the superconductor gap. We would like to point out that the Raman spectroscopy measurements are not sensitive to the phase of the order parameter and, therefore, there is no way to distinguish between $d_{x^2-y^2}$ and a strongly anisotropic $s$-wave gap symmetry.

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